

Table S1. Rate constants for water substitution at  $\mathbf{Rh}_3^+$  by methanol- $d_4$ .

$[Rh_3(\mu_3-O)(\mu-O_2CR)_6(OH_2)_3]^+$ $(\mathbf{Rh}_3^+)$	T (K)	k ( $s^{-1}$ )
<b>R = CH<sub>2</sub>CH<sub>3</sub></b>	266.0	8.6 ( $\pm 0.1$ ) x 10 <sup>-5</sup>
	276.4	4.52 ( $\pm 0.07$ ) x 10 <sup>-4</sup>
	278.4	6.89 ( $\pm 0.07$ ) x 10 <sup>-4</sup>
<b>R = CH<sub>3</sub></b>	272.5	1.21 ( $\pm 0.02$ ) x 10 <sup>-4</sup>
	276.3	2.03 ( $\pm 0.05$ ) x 10 <sup>-4</sup>
	276.0	1.88 ( $\pm 0.02$ ) x 10 <sup>-4</sup>
	281.0	4.55 ( $\pm 0.04$ ) x 10 <sup>-4</sup>
	281.1	4.74 ( $\pm 0.03$ ) x 10 <sup>-4</sup>
	273.2	3.3 ( $\pm 0.1$ ) x 10 <sup>-5</sup>
<b>R = CH<sub>2</sub>CH<sub>2</sub>Cl</b>	276.2	6.6 ( $\pm 0.3$ ) x 10 <sup>-5</sup>
	276.4	6.69 ( $\pm 0.06$ ) x 10 <sup>-5</sup>
	279.6	1.05 ( $\pm 0.04$ ) x 10 <sup>-4</sup>
	283.0	1.73 ( $\pm 0.04$ ) x 10 <sup>-4</sup>
	276.3	1.64 ( $\pm 0.01$ ) x 10 <sup>-5</sup>
	283.2	4.74 ( $\pm 0.02$ ) x 10 <sup>-5</sup>
<b>R = CH<sub>2</sub>Cl</b>	290.8	1.75 ( $\pm 0.03$ ) x 10 <sup>-4</sup>
	276.3	5.3 ( $\pm 0.7$ ) x 10 <sup>-7</sup>
	302.9	5.3 ( $\pm 0.2$ ) x 10 <sup>-5</sup>
<b>R = CHCl<sub>2</sub></b>	313.5	2.24 ( $\pm 0.05$ ) x 10 <sup>-4</sup>